

Amendments to the Specification:

Please delete the title and insert the following in lieu thereof::

FLUORINATED THERMOSET POLYURETHANE ELASTOMERS PREPARED FROM
POLYETHER PREPOLYMERS FORMED FROM MONO-SUBSTITUTED FLUORINATED
OXETANE MONOMERS

Please replace the paragraph beginning at page 2, line 2, which starts with "This application is a" with the following amended paragraph:

~~This application is a Continuation In Part application of our copending application SN 08/206,859, filed March 7, 1994, which in turn is a Continuation application of SN 07/911,461, filed July 7, 1992, currently abandoned~~ U.S. Application No. 09/521,263, filed March 8, 2000, is a continuation application of Application No. 08/477,168, which is a divisional application of copending Application No. 08/371,914, filed January 12, 1995 (now U.S. Patent No. 5,807,977), which is a continuation-in-part application of Application No. 08/206,618, filed March 3, 1994 (now abandoned), which is a continuation application of Application No. 08/080,614, filed June 21, 1993 (now abandoned), which is a continuation-in-part application of Application No. 07/911,461, filed July 10, 1992 (now abandoned).

Please replace the paragraph beginning at page 7, line 29, which starts with "Falk et al." with the following amended paragraph:

Falk et al. (US 5,097,048) disclose the synthesis of bis-substituted ~~perfluoroalkyl oxetane monomer~~ oxetane monomers having perfluoro-terminated alkyl group side chains from bis-haloalkyl oxetane, the ~~perfluoroalkyl~~ glycols having perfluoro-terminated alkyl group side chains derived therefrom, including related thiol and amine linked glycols and dimer diols. Most of the fluorinated side-chains are attached to the glycol unit by either a thio, an amine or a

sulfonamide linkage. Only a few of their examples describe glycols with ~~fluorinated~~ perfluoro-terminated alkoxymethylene side-chains.

Please replace the paragraph beginning at page 8, line 2, which starts with "Falk et al." with the following amended paragraph:

Falk et al. (EP 03 48 350) report that their process yields ~~perfluoroalkyloxymethylene~~ perfluoro-terminated alkoxymethylene neopentyl glycols composed of a mixture of (1) approximately 64% of the bis-substituted ~~perfluoroalkyl~~ perfluoro-terminated alkyl neopentyl glycol, and (2) approximately 36% of a mono-substituted ~~perfluoroalkyl~~ perfluoro-terminated alkyl neopentyl glycol product with a pendant chloromethyl group. Evidently, the mono-substituted product results from incomplete substitution of the second chloride on the sib-chloroalkyl oxetane starting material. Consequently, as noted from the Zisman and Pittman work above, the presence of the -CH₂Cl as a side-chain significantly increases the surface energy of coatings made from these polymers thus reducing the hydrophobicity and oleophobicity of the coating.

Please replace the paragraph beginning at page 8, line 14, which starts with "Not surprisingly, it is" with the following amended paragraph:

Not surprisingly, it is understandable that Falk et al. (US 5,097,048) discourages the use of the mono-substituted glycol for the preparation of low surface energy coatings, since the monosubstituted glycol as produced from bis-chloroalkyl oxetanes would necessarily have a residual chloromethyl group still attached to the 3-carbon because of the incomplete substitution of the bis-haloalkyl moieties on the starting material. Accordingly, their teaching that the polymer derivatives from mono-substituted glycols do not produce a coating exhibiting the desired properties, ~~as compared to the same extent as~~ as compared to the same extent as coatings derived from bis-substituted glycols, ~~is a direct result of the increase in free energy associated with the remaining~~

chloromethyl group on Falk's mono-substituted glycol is premised on a lower free surface energy for the bis-sustituted compounds as compared to Falk's mono-substituted compounds (Falk, US 5,097,048, column 1, lines 43-50). However, they ignore the fact that the residual chloromethyl group may serve to increase the free surface energy of the Falk mono-substituted compound more so than the fact it is only mono-substituted in a Rf function.

Please replace the paragraph beginning at page 8, line 26, which starts with "Moreover, the reference cited" with the following amended paragraph:

Moreover, the reference cited by Falk et al. in the '048 patent, J. Org. Chem., 45 (19) 3930 (1980), stating at line 33 that "mono-fluoroalkyl oxetanes containing oxygen have been reported" is misleading in that the reference cited discusses oxetanes substituted with -CH₂F side chains (i.e., (monofluoro)alkyl oxetanes) and not alkoxymethylene side chains with terminal prefluoroalkyl groups. Hence, this reference will not lead to materials with low surface energies and is not relevant to the compounds of this invention.

Please replace the paragraph beginning at page 8, line 34, which starts with "Falk et al. (US 5,097,048)" with the following amended paragraph:

Falk et al. (US 5,097,048 5,045,624) teaches preparation of dimers with fluorinated side-chains having thio linkages, but not of dimers with fluorinated ether side-chains. This is because his synthesis route for preparing dimers with thio linkages cannot be used for the synthesis of dimers with ether linkages. In other words, Falk et al. does not teach preparation of long chain polyethers with fluorinated ether side-chains.

Please replace the paragraph beginning at page 9, line 20, which starts with "None of the Falk et al." with the following amended paragraph:

None of the Falk et al. references teach or show a homo-prepolymer or co-prepolymer made from ~~bis-perfluoroalkoxymethylene~~ bis-perfluoro-terminated alkoxymethylene oxetanes, nor polyurethanes derived ~~therefrom~~ therefrom or from the corresponding glycols. All of their polyurethanes are made directly from the thiol linked monomers and dimers and not via a prepolymer intermediate. In the examples provided in Falk et al. (US[[.]] 5,097,048), particularly where the ~~fluorinated~~ perfluoro-terminated side-chains are large and for all of the dimers, all have thiol linkages; no ether side-chains are shown. The polyurethanes disclosed by Falk et al. (US 4,898,981) are made from the ~~perfluoroalkylthio~~ perfluoro-terminated alkylthio neopentyl glycol. They do not teach, show or suggest producing a polyurethane from the ~~perfluoroalkoxy~~ perfluoro-terminated alkoxys neopentyl glycol monomer, nor do they suggest, teach or show the types of prepolymers and polymers that can be prepared from the mono-substituted 3-perfluoroalkoxymethylene-3-methyl oxetanes (i.e., FOX monomers). However, Falk et al. (US 5,097,048) in their Example 12 show a polyether prepolymer prepared from a bis-substituted perfluoroalkylthio oxetane. The prepolymer obtained was a white waxy solid, clearly not an elastomer. No characterization as to ~~molecular weight~~, nature of the end groups, polydispersivity, equivalent weights, etc. of the [[the]] waxy solid was given. Absent such a characterization, it is unknown as to whether Falk et al.'s material may be further reacted with an isocyanate to produce a polyurethane polymer. No examples of the preparation of a polymer from any prepolymer is given.

Please replace the paragraph beginning at page 18, line 30, which starts with "Surprisingly, and contrary to the teachings" with the following amended paragraph:

Surprisingly, and contrary to the teachings of the prior art, two fluorinated side chains are not necessary to impart high levels hydrophobic and low surface energy properties. The art teaches that the more fluorine, the better the properties, ~~but did not recognize that the~~ presence ~~presence~~ of two identical perfluoro-terminated side chains leads to steric hindrance and formation of crystalline materials, a morphology which makes further processing difficult. In

contrast, we believe the asymmetry presented by the single (mono) group having fluorinated substituents of the FOX monomers of our invention which upon polymerization prevents the regularity in packing and results in amorphous prepolymers.

Please replace the paragraph beginning at page 7, line 29, which starts with "Falk et al." with the following amended paragraph:

Please replace the paragraph beginning at page 22, line 4, which starts with "This phase transfer catalyzed" with the following amended paragraph:

This phase transfer catalyzed intramolecular cyclization has not been attempted before for the production of BrMMO. Prior attempts have resulted in low yields of the cyclic products (12-60%) due to two principle side reactions. The first side reaction is a ~~1,4-elimination~~ with the formation of a stable olefin, 3-bromo-2-methylprop-1-ene, in preference to the relatively more strained oxetane ring. A second competing reaction is the formation of the dimer and trimer.

Please replace the paragraph beginning at page 22, line 11, which starts with "These side reactions are" with the following amended paragraph:

These side reactions are minimized by choosing an appropriate solvent. We have found that n-butyl chloride and carbon tetrachloride provided yields of BrMMO on the order of 94-97%. Other solvents investigated, such as ~~acetonitrile~~, toluene, ~~DMF~~, ligroine, 1,1,2-trichloroethane, benzene, n-hexane and hexanes gave more complex reaction mixtures containing both competing side reactions of elimination and dimerization.

Please replace the paragraph beginning at page 27, line 29, which starts with "The pre-monomer of this invention" with the following amended paragraph:

The pre-monomer of this invention, BrMMO, is particularly well suited for the synthesis of the oxetane monomers in that the BrMMO is uniquely clean and free of by-products resulting from its novel synthetic pathway. ~~An example of the latter is the p-toluene sulfonate derivative of 3-hydroxymethyl 3-methoxyloxetane. A high yield of the oxetanes having pendant alkoxymethylene groups with terminal perfluorinated alkyl groups is obtained.~~

Please replace the paragraph beginning at page 35, line 19, which starts with "The polymerization of FOX" with the following amended paragraph:

The polymerization of FOX monomers occurs by cationic ring-opening reaction. ~~The mechanism for which is presented below:~~

Please delete all of the figures and the sentence "See Fig. 2." after the paragraph beginning at page 35, line 19, which starts with "The polymerization of FOX"

Please replace the paragraph beginning at page 40, line 8, which starts with "The surface energy of the" with the following amended paragraph:

The surface energy of the FOX/THF coprepolymer as a cured polymer is lower than that of polytetrafluoroethylene (Teflon) and is attributed to the presence of the fluorine in the side-chains rather than the backbone. It is noteworthy that the FOX/THF prepolymer is formed from the mono-substituted FOX monomers of this invention and the surface energy is comparable to that of the polymers formed from the sib-substituted monomers described in the background. Consequently, the FOX monomer is preferable to the *bis*-perfluoroalkyl monomers of the background, not only because the mono-substituted FOX monomers product products

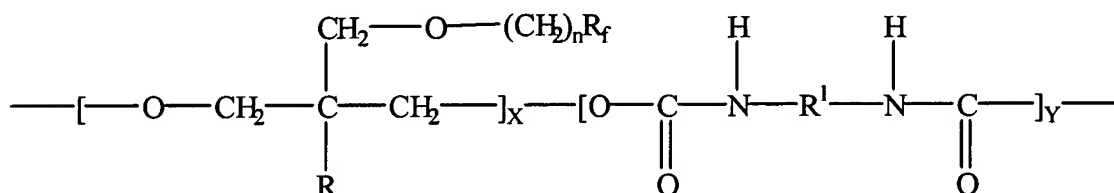
having comparable or better surface energy, but also because of its ability to copolymerize with THF, thus reducing the starting materials cost. Even though we have significantly reduced the amount of fluorine in the FOX/THF co-prepolymer by introduction of the THF segments, it has thus far been determined that when the FOX/THF copolymer contains up to about 65% THF, no significant reduction in surface energy is observed in polyurethane elastomers as compared to the ~~polymers~~ elastomers prepared from the mono-substituted FOX monomers.

Please replace the paragraph beginning at page 45, line 1, which starts with "The number average" with the following amended paragraph:

The number average molecular weights of FOX/THF co-prepolymers, as determined by GPC, were between 10,000 and 14,000, whereas polydispersities were between 1.5 and 2.1. The co-prepolymers exhibited unimodal molecular weight distribution, and with the exception of 90:10 7-FOX/THF co-prepolymer, FOX/THF co-prepolymers were free of cyclic oligomers. The equivalent weight of 60:40 7-FOX/THF co-prepolymer, determined by ¹H NMR employing TFAA end group analysis, was 6,230. The equivalent weight of the same co-prepolymer by p-toluenesulfonyl isocyanate/dibutyl amine titration method was 5,890. The glass transition temperature of the 60:40 7-FOX/THF co-prepolymer by DSC analysis was -43°C; no other transitions were detected between -100°C and +130°C. By comparison, the glass transition temperature of the 7-FOX homo-prepolymer was -42°C. This result indicates that the glass transition temperature of the co-prepolymer is not affected by the incorporation of THF, ~~and that the prepolymer is a random copolymer~~. If the prepolymer was a block copolymer or a mixture of two homopolymers, more than one transition would be observed. This was further confirmed by the dynamic mechanical property measurements of 60:40 7-FOX/THF co-prepolymer where only one transition (T_g) was observed at -41°C. It should be noted that the formation of a random copolymer between FOX and THF monomers is unexpected since the vast difference in the reactivity of these two monomers would dictate the formation of a block copolymer or two homopolymers.

Please delete the structure after the paragraph beginning at page 48, line 3, which starts with "The fluorine-containing thermoset"

Please add the following new structure after the paragraph beginning at page 48, line 3, which starts with "The fluorine-containing thermoset":



Please replace the paragraph beginning at page 48, line 13, which starts with "where: n is 1-3" with the following amended paragraph:

where: n is 1-3;

R is methyl or ethyl;

R_f is a linear or branched perfluorinated alkyl group having 1-20 carbons, or an oxaperfluorinated polyether having from about 4-20 carbons

X is 10-200 and Y is [[1-10]] 2-50

Please replace the paragraph beginning at page 48, line 20, which starts with "R¹ is an alkyl or aryl" with the following amended paragraph:

R¹ is ~~an alkyl or aryl functional group~~ a divalent hydrocarbyl radical, examples of which include the following structures:

Please replace the paragraph beginning at page 48, line 35, which starts with "The resulting polyurethane" with the following amended paragraph:

The resulting polyurethane is tack-free opaque, generally insoluble in organic solvents and has a glass transition temperature between -40°C and -47°C. Contact angle measurements of between 110° and 145° with distilled water and surface energy measurements of 13.8 - 15.2 ergs/cm² indicate that the surface wettability (~~hydrophobicity~~) and non-adhesive characteristics of the elastomer of this invention are greater than those measured for Teflon (110° contact angle and 18.5 ergs/cm² surface energy). We have observed that as the size of the side-chain on the FOX polymers increases, hydrophobicity increases as well (see Table 3). As indicated above, the 145° contact angle of the polyurethane derived from the 15-FOX prepolymer is characteristic of the extreme hydrophobicity of the FOX polymers of this invention. The 145° contact angle of the 15-FOX polyurethane is one of the highest ever observed.

Please replace the table beginning at page 51, line 3, with the following amended table:

MATERIAL	SURFACE ENERGY (ERGS/CM²)
Teflon	18.5
Polydimethylsilanes <u>Polydimethylsiloxanes</u>	24
Polyethylene	31
Polytrichlorofluoroethylene	31
Polystyrene	33-35
Poly(methyl-methacrylate)	33-34
Nylon 66	46

Please replace the paragraph beginning at page 52, line 2, which starts with "The crosslinking agents" with the following amended paragraph:

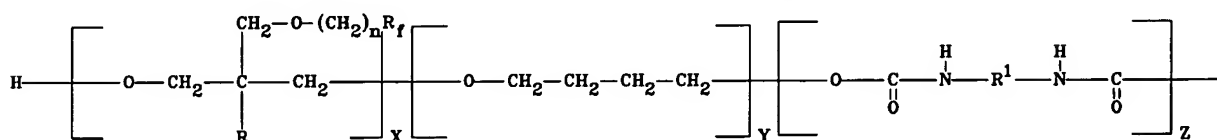
The crosslinking agents normally used are low molecular weight polyols or polyamines such as trimethylolpropane, pentaerythritol, Isonol® 93, a polyether polyol which is commercially available from Dow Chemical Co., trimethylolethane, triethanolamine, Jeffamines, 1,4-butanediamine, xylene diamine, diethylenetriamine, methylene dianiline, diethanolamine, etc. The preferred crosslinking agents are trimethylolpropane, Isonol 93®, a polyether polyol which is commercially available from Dow Chemical Co., methylene dianiline, and Jeffamines. The mechanical properties of an elastomer can be altered by varying the amount of crosslinking agent. Generally, increasing the amount of crosslinking agent in a polyurethane formulation leads to materials with higher modulus and improved chemical and abrasion resistance. The amount of crosslinking agent can be varied from 0-15% by weight, however, the preferred amount is between 1.5% and 5% by weight.

Please replace the paragraph beginning at page 52, line 25, which starts with "The polyisocyanates useful" with the following amended paragraph:

The polyisocyanates useful in the synthesis of FOX polyurethanes are: hexamethylene diisocyanate (HDI), Isophorone diisocyanate (IPDI), Methylene diphenylisocyanate (MDI), saturated MDI (Des-W), polymeric MDI, which are available from Dow Chemical Co. under the trademark ISONATE, a line of low-functionality isocyanates, (Isonates), toluene diisocyanate (TDI), polymeric HDI, which are available from Mobay Corporation, a Bayer Company, under the trademarks DESMODUR N-100, a solvent-free, aliphatic polyisocyanate resin based on hexamethylene diisocyanate, and DESMODUR N-3200, an aliphatic polyisocyanate resin based on hexamethylene diisocyanate, (N-100 and N-3200), cyclohexylene-1,4-diisocyanate, and 2,2,4-trimethylhexamethylene diisocyanate. The NCO:OH ratio can be from 1.1 to 0.9, however the preferred ratio is 1.02.

Please add the following new paragraph after the paragraph beginning at page 56, line 1, which starts with "FOX/THF co-prepolymers may be also":

The fluorinated thermoset polyurethane elastomers prepared from the FOX/THF co-prepolymers of the present invention having the following general structure:



wherein:

n is 1-3;

R is selected from the group consisting of methyl and ethyl;

R_f is selected from the group consisting of perfluorinated alkyls having 1-20 carbons, or an oxaperfluorinated polyether having from about 4-20 carbons;

R¹ is a divalent hydrocarbyl radical;

X is 1-20;

Y is 10-150; and

Z is 2-50.

Please replace the paragraph beginning at page 56, line 11, which starts with "The FOX/THF co-prepolymers described" with the following amended paragraph:

The FOX/THF co-prepolymers described in this invention are difunctional and have terminal hydroxy groups. These hydroxy groups are primary and react readily with isocyanates to form high molecular weight polyurethane elastomers. In a typical reaction, the co-prepolymer is reacted with an equivalent amount of polyisocyanate in the presence of a catalyst and a crosslinking agent to form a 3-dimensional polymer network. If the functionality of the polyisocyanate is 2, then a crosslinking agent is needed to form a crosslinked network. However, if the functionality of the polyisocyanate is >2, then no crosslinking agent is needed. In some cases, additional crosslinking agent is added to improve the chemical and abrasion

resistance of the polymer. The crosslinking agent normally used is a low molecular weight polyol or polyamine such as trimethylolpropane, Isonol 93, Jeffamines, trimethylolethane, pentarerythritol, triethanol-amine, diethanolamine, 4,4-methylene dianiline, MOCA, 1,4-butanediamine, diethylenetriamine, xylene diamine, etc. The preferred crosslinking agents are Isonol 93, trimethylolpropane and Jeffamines. The preferred catalyst is dibutyltin dilaurate, however other catalysts such as triethylamine, DABCO, Ferric acetylacetonate, triphenyl bismuth, tin octanoate, lead octanoate, etc., can also be used. The catalyst concentration is normally between 0.1 and 0.2% by weight. The polyisocyanates useful in the synthesis of fluorinated polyurethanes are hexamethylene diisocyanate (HDI), Isophorone diisocyanate (IPDI), 4,4-methylene diphenylisocyanate (MDI), polymeric MDI, which are available from Dow Chemical Co. under the trademark ISONATE, a line of low-functionality isocyanates, (Isonates), toluene diisocyanates, saturated MDI (HMDI), polymeric HDI, which are available from Mobay Corporation, a Bayer Company, under the trademarks DESMODUR N-100, a solvent-free, aliphatic polyisocyanate resin based on hexamethylene diisocyanate, and DESMODUR N-3200, an aliphatic polyisocyanate resin based on hexamethylene diisocyanate, (N-100 and N-3200), and trimethylhexane diisocyanate. The NCO:OH ratio can be from 1.1 to 0.9, but the preferred ratio is 1.02. Bulk materials are prepared by casting the above formulation in a mold, degassing the mixture under reduced pressure for 15 mins, and then curing it in an oven at 65°C for 16 h. If a thin film is desired, a solvent, like THF, is added to reduce the viscosity, and the mixture is spread over the substrate with a doctor's blade to form a film of desired thickness. Alternatively, the substrate can be dip-coated or spray coated, then cured in an oven at 60°C - 65°C.

Please replace the paragraph beginning at page 58, line 10, which starts with "An elastomer that has been" with the following amended paragraph:

An elastomer that has been characterized in detail is prepared from 60:40 7-FOX/THF co-prepolymer, Isonol 93 and HMDI, in the presence of dibutyltin dilaurate catalyst.

The candidate material, a 3 x 5 x 0.2 inch³ sample, is an opaque elastomer. The static contact angle of this material with doubly distilled water is 117°. By comparison, static contact angles of water with Teflon and 7-FOX polyurethane are 110° and 119°, respectively. The surface energy of the candidate material, as determined by the method of Wu et al., is 13.5 erg/cm². This value is considerably lower than that of Teflon (18.5 ergs/cm²), but similar to that of 7-FOX polyurethane (13.2 ergs/cm²). The above results indicate that polyurethane prepared from 7-FOX/THF co-prepolymer is comparable in release characteristics and hydrophobicity to 7-FOX polyurethane, but is substantially more ~~hydrophobic~~ non-wettable and non-stick than Teflon. In view of the reduced amount of fluorinated starting materials required to assemble the mono-substituted FOX monomers of this invention and further in view of the reduced amount of FOX monomer required in order to assemble a FOX/THF co-prepolymer, there is a significant cost savings over prepolymers assembled from the bis-substituted monomers or prepolymers assembled solely from the FOX monomers.